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(54) **Quantum sized activator doped semiconductor particles.**

(57) Luminescent layer comprising activator doped semiconductor nanoparticles of a size ( $< 100\text{\AA}$ ) which exhibit quantum effects. The nanoparticles are grown and doped within a polymer matrix, or precipitated and coated with a surfactant.

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BACKGROUND AND SUMMARY OF THE INVENTION

This invention relates to semiconductor materials and particularly to a layer of quantum sized activator doped semiconductor particles and to methods for manufacturing these particles.

5 By making semiconductor particles small enough to show quantum confinement effects and doping them with a luminescent activator element (referred to as "doped nanocrystals"), new optical properties are created which differ from those of chemically identical bulk material and from the quantum confined host material alone. An activator doped and quantum confined host material was made (ZnS:Mn) that demonstrates blue (shorter wavelengths) shift in the excitation wavelengths of the activator. These systems also display a dramatic decrease in the time for luminescence decay with an efficiency and brightness comparable to bulk (ZnS:Mn) phosphors. These new material characteristics indicate a fundamental change in optical properties and this is the first time materials exhibiting these characteristics have been made. The invention also relates to methods to produce this material and to other unique properties, such as reduced excitation voltages for (flat panel) cathode ray tubes.

15 It has been recognized that when the radius of a semiconductor crystallite is near that of the Bohr radius of the exciton, there is a quantum size effect and its electronic properties change. Most of the II-VI and some III-V and group IV semiconductors have been prepared as quantum sized particles and demonstrate quantum size effects in their physical properties. The size at which the particles demonstrate changes in their bandgap from the quantum size effects vary with the intrinsic electronic structure of the compound but typically appear when below 100 Å in diameter. To exhibit quantum size effects it is also necessary for the particles to remain isolated from one another, if allowed to aggregate the material exhibits bulk properties despite the small size of the individual particles.

Undoped quantum size particles have previously been prepared in several ways: spontaneous nucleation in solution, heterogeneous growth from a substrate material, growth within a micelle, growth in solution atop a carrier particle, nucleation in a sputtering chamber, and laser ablation. The present invention is directed towards the doping of a quantum sized semiconductor host material with an activator element which demonstrates new material properties.

Possible applications for new materials based on the concepts and materials described in this application include:

- 30 - Luminescent phosphors for use in cathode ray tubes and lights.
- Thin films for electroluminescent displays.
- Lasing phosphors.
- The use of luminescent activators and magnetic particles for magneto-optical recording and displays.
- Lower voltage phosphors for flat cathode ray tubes
- 35 - Markers for medical diagnosis

The present application also provides methods for manufacturing quantum sized doped semiconductor particles. The methodology is particularly advantageous in that it provides a relatively simple approach to the manufacture of doped quantum sized semiconductor particles at room temperature. Furthermore, the particles so produced may be dispersed within a polymer matrix and the reaction which forms the doped particles may take place in the polymer matrix. Thereafter, the polymer matrix maintains the doped particles separate from one another so that they maintain their quantum physical effects without agglomeration.

To maintain the separation for quantum confinement in precipitated particles, it is also desirable to add a material which coats the surface of the particles and provides a barrier to agglomeration. These molecules are commonly referred to as surface active agents - surfactants. The requirements of a surfactant for the present system are straightforward:

1. must be soluble in hydrocarbon solvents
2. must not participate in the chemical reactions to dope or form the ZnS
3. must have an ultraviolet absorption below the absorption edge of the host matrix (e.g. ZnS). This requirement may be ignored for long wavelength or non-optical applications.

50 It is the ultraviolet absorbance which excludes most Known surfactants, nevertheless it is believed that there are many molecules which could suffice. The surfactant preferably used in this invention is poly-(methyl methacrylate) (PMMA) and its monomer, methacrylic acid. PMMA has been studied as a surfactant and has demonstrated both physical adsorption (thermodynamic driven) and chemical adsorption (hydrogen bonding with C=O group in polymer) onto oxide surfaces.

55 The doped nanocrystals produced by the present invention have a luminescent efficiency which is relatively high for films prepared at room temperature. Normally, thin films of bulk ZnS:Mn used in electroluminescent devices yield high efficiency when prepared above temperatures of 350 °C. For powder phosphors, this temperature is frequently as high as 1000 °C. However, high processing temperatures

would change the morphology of quantum sized particles and destroy their properties. The new doped nanocrystals also emit light significantly faster (shorter luminescent decay time) than that observed with corresponding bulk material. This faster luminescent decay time in a nanocrystal provides advantage over bulk material for application where speed is important, i.e. faster phosphors for next generation TV's and displays. It is believed that this characteristic has not been observed before.

#### BRIEF SUMMARY OF THE DRAWINGS

For a better understanding of the invention, reference is made to the following drawings which are to be taken in conjunction with the detailed specification to follow:

Figure 1 is a graph of UV absorption Abs. wavelength  $\lambda$  for doped nanoparticles made in accordance with the invention;

Figure 2 is a graph of intensity I of the photoluminescence of the dopant emission vs. wavelength  $\lambda$  for the doped nanoparticles;

Figure 3 is a graph showing the effect of UV curing on the intensity I of the luminescence of encapsulated doped nanoparticles;

Figure 4 is a graph of the luminescent decay of encapsulated doped nanoparticles.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following illustrates the steps of a process for the preparation of (manganese) doped zinc sulphide quantum size particles.

The process begins at a step 1 wherein zinc chloride and manganese chloride are dissolved in water at room temperature. At this step a compound containing one of the components of the host and a compound containing the dopant are dissolved at room temperature in a suitable solvent, in this case water. The quantities used herein are 0.09 gram zinc chloride and 0.01 gram manganese chloride dissolved in 30 ml of distilled and de-ionized water, thus an extremely dilute solution of  $2.2 \times 10^{-2}$  M (moles/liter)  $\text{ZnCl}_2$  and  $2.7 \times 10^{-3}$  M  $\text{MnCl}_2$ . Added to the dissolved solution at a step 2 is 1.35 grams of polyethylene oxide ( $-\text{CH}_2\text{CH}_2\text{O}-$ )<sub>n</sub> powder (PEO) [avg. molecular weight 200,000]. The solution was stirred for several hours so as to allow the polyethylene oxide to fully dissolve. Thereafter at a step 3 the dissolved solution was cast onto a flat surface in the form of a glass plate. At a step 4 the cast solution was dried under flowing nitrogen. The drying step 4 can take place under air, however flowing nitrogen speeds the process and helps prevent crystallization of the PEO. After the drying is complete, at a step 5, the film (of approximate thickness of 1 mm) is peeled off of the glass plate and cut into suitable sized coupons and allowed to dry on both sides.

The coupons are thereafter ready to be placed in a reactive solution, again at room temperature, of a solvent at a step 6 which will dissolve a sulphur containing compound, but will not dissolve the PEO matrix. A suitable solvent is the hydrocarbon solvent cyclohexane ( $\text{C}_6\text{H}_{12}$ ). The sulphur bearing compound is hexamethyldisilthian  $\text{S}(\text{Si}(\text{CH}_3)_3)_2$  which will dissolve in the cyclohexane and which will diffuse through the PEO matrix and readily cleave off its sulphur. The coupon is left in the solution of step 6 for a period of days or weeks as the reaction proceeds slowly and the doped particles grow within the PEO matrix. The reaction will proceed to grow quantum sized manganese doped zinc sulphide particles. As an alternative to hexamethyldisilthian, hydrogen sulfide gas ( $\text{H}_2\text{S}$ ) may be bubbled into the cyclohexane. After the reaction is complete at a step 7 the coupons are removed and dried in flowing nitrogen. The coupon remains intact but contained within its polymer matrix are the manganese doped zinc sulphide particles of approximately 20-100 Å which have a doping % of Mn of 0.5-1.0%. The polyethylene matrix serves to prevent the particles from clumping together which will ruin the quantum effects.

The incorporation of a luminescing dopant in a nanocrystal yields characteristic emission of the dopant and high luminescent efficiency. For example, Mn in ZnS has a yellow orange emission while Tb doped in ZnS emits green. To obtain yellow orange emission in Mn doped ZnS, the film containing ZnS:Mn particles is excited with a wavelength of 300 nm. However, if the detector is kept at the yellow-orange wavelength and the wavelength of the exciting light is varied, the orange emission due to the  $\text{Mn}^{2+}$  activator, peaks when energy of the exciting light approaches the bandgap energy of the ZnS particle. The process of monitoring the luminescence using the emission associated with an external impurity is referred as the Photoluminescence excitation (PLE) method. For example the band gap of bulk ZnS is about 339 nm and from PLE measurements the bandgap obtained is 340 nm. Similarly for nanosized particles the bandgap energy has increased to about 310 nm and the peak of the excitation (PLE peak) is 309 nm. Thus with a simple technique of measuring PLE, one can obtain the bandgap of the nanocrystals. This permits the distinguishing of the contribution of the various size of particles to the total luminescent intensity. Besides

obtaining the band gap, it can be demonstrated that the Mn ion is an integral part of the ZnS nanocrystal, because it is only excited via the ZnS bandgap. Since in nanocrystals the bandgap is size dependent, the PLE technique is useful to obtain the sizes and their distribution.

Figure 1 is a graph of ultraviolet (UV) absorption A plotted against wavelength (in nm) for doped nanoparticles grown for varying periods of time (i.e. the length of time the coupons are left in the reactive solution). As can be seen the unreacted solution (curve d) shows no peak across the wavelengths of interest. At 5 days of growth (curve b) a peak of 261 nm is seen and after 35 days of growth (curve d) a peak at 277 nm is shown. Curve c (21 days) is in between. This indicates that the bandgap narrows and the size of the particles increases as they are left in the reactive solution. Thus, the size of the particles may be readily adjusted by reaction time. Of course if the size becomes too large the quantum effects will diminish or become negligible. Figure 2 is a graph of photoluminescent excitation (I (arbitrary units) vs. wavelength  $\lambda$  (in nm) for the  $Mn^{2+}$  and again shows a shift towards peaks at longer wavelengths as a function of time in the reactive solution, increases which demonstrates the increasing size of the doped nanocrystals as the reaction progresses.

In this reaction, nitrates such as zinc nitrate, manganese nitrate and certain selected acetates may be utilized in a suitable solvent. Many other solvents could be substituted for the distilled water in the above-described methodology. It is only necessary that the solvent dissolve both the chemical compound containing the first component of the host, the compound containing the dopant and the PEO. Suitable alternative solvents are alcohol and methyl ethyl ketone. The molecular weight and the concentration of the PEO dissolved in the water is not extremely critical. It is only necessary that these parameters be adjusted so that the PEO will dry and that it can be peeled off in coupons so as to be placed in the reactive solution.

In addition to the manganese doping of zinc sulfide the present process is also suitable for doping zinc sulphide with terbium, the starting component is changed to  $TbCl_3$ . Additionally, other semiconductor host materials may also be prepared and doped with suitable activators. Such host materials may be zinc selenide ( $ZnSe$ ) zinc telluride ( $ZnTe$ ) cadmium sulfide ( $CdS$ ) and cadmium selenide ( $CdSe$ ) may also be utilized in similar reactions. Finally dopants such as copper, silver, thallium, cerium, chromium, titanium and other rare earth elements may be utilized.

An alternative process will be presented in hereinafter. The starting solution at a step a contains pure diethylzinc ( $(C_2H_5)_2Zn$ , CAS number [557-20-0]) dissolved in toluene (Anhydrous,  $C_6H_5CH_3$ , CAS no. [108-88-3]) so that the final reaction concentration of zinc is  $5 \times 10^{-3}$  M. The diethylzinc can also be obtained by a Grignard reaction. The surfactant, poly(methyl methacrylate) (medium molecular weight powder, approximately 145,000),  $[H_2C=C(CH_3)(COOCH_3)]_n$ , CAS no. [9011-14-7], (0.28g dissolved in 20 ml toluene)), is added to the diethylzinc solution at a step b. It takes approximately 12-18 hours for the PMMA to dissolve.

Separately, the diethylmanganese was prepared by the Grignard reaction of 1.3 ml of manganese chloride ( $MnCl_2$ , CAS no. [7773-01-5]) (0.122g dissolved in 17ml tetrahydrofuran at a step c)) (anhydrous,  $C_4H_8O$ , CAS no. [109-99-9]) with 10 ml of ethylmagnesium chloride (2.0M solution in tetrahydrofuran,  $C_2H_5MgCl$ , CAS no. [2386-64-3], (diluted 1:100 in tetrahydrofuran at a step d)). This amount of manganese would correspond to approximately 10 atomic % if all manganese chloride was converted to diethylmanganese and all was incorporated in the ZnS. A stoichiometric excess of ethylmagnesium chloride is used to drive the reaction at a step e to completion. The reaction product is orange in colour but turns brown with time - as the diethylmanganese decomposes.

In another separate reaction at a step f, hydrogen sulfide gas ( $H_2S$ , gas, CAS no. [7783-06-4]) is bubbled through 23.72 ml of toluene for approximately 5 minutes and then stopped, this time is considered sufficient for the room temperature equilibrium concentration of hydrogen sulfide to be solubilized (approximately  $6.32 \times 10^{-4}$  moles/ml at  $20^\circ C$ ). This provides a final concentration of sulfur to the reaction of  $1 \times 10^{-1}$  M. Note that  $H_2S$  should not be bubbled into the reaction as bubbling  $H_2S$  directly into the reaction would cause non-quantum-sized particles to form on the bubbles at the gas/liquid interface. The precipitation occurred instantaneously at a step g when after the addition of the diethylmanganese solution to the previous solution of diethylzinc and PMMA, the solubilized hydrogen sulfide was also added at step f. The reaction is in evidence first by the observation of evolved gases (probably ethylene) from a bubbler attached to the reactor, and second by the change in the solution from transparent to translucent, a result of particle agglomeration into flocs large enough to scatter light. The precipitated particles are quantum sized ( $<100\text{\AA}$ ) ZnS:Mn coated with PMMA with a dopant concentration of 0.5-1.0%. After the precipitation the particles may be washed in any solvent suitable to remove reaction byproducts from the particles. At a step h the encapsulated particles are cured by UV exposure.

Another unique characteristic of this material is the effect of the surfactant, and the ultraviolet curing of the surfactant, on the light emission. The brightness was visibly improved when the precipitated particles were exposed to ultraviolet light (300 nm) over several minutes. Figure 3 demonstrates that after exposure

the intensity  $I$  (arbitrary units) of the orange emission improves when all other experimental conditions are kept the same (curve A: no cure; curve B: 1.25 hr cure; curve C: 3.25 hr cure). The samples show a decreased rate of improvement with time. Bulk ZnS:Mn samples were similarly tested after coating with the same surfactant in toluene, settling and drying. In contrast, the luminescent intensity of the bulk ZnS:Mn decreases with exposure time.

These characteristics were also observed on samples in which ZnS quantum sized particles were doped with manganese and using methacrylic acid ( $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{COOH}$ , CAS no. [79-41-4]) as the surfactant rather than poly(methyl methacrylate) polymer, and these characteristics have since been demonstrated in earlier samples of both medium (145,000) and low (12,000) molecular weight poly(methyl methacrylate).

The cause of UV curing and why it is different in bulk and nanometer sized particles is not well understood. The ultraviolet curing of the surfactant may cause physical changes such as polymerization of the monomer, increased cross-linking in the polymer, which results in passivation of terminal chemical sites on the particles. Normal expectations are that the increased molecular mass upon curing leads to increase surfactant absorbance and a decrease in light emission as seen in the bulk ZnS:Mn powder. It is believed that UV curing is providing surface passivation of the nanocrystals through photopolymerization. The increase in light emission is probably related to decrease of the surface related non-radiative processes. It may be possible to replicate this effect by another surfactant or a purely chemical treatment.

The nanoparticles produced by the methodology comprise doped semiconductor particles of from 20-100Å in size with a coating of surfactant. The thickness of the coating depends on the physical characteristics of the surfactant used, methacrylic acid will provide the thinnest coating ( $\approx 10\text{\AA}$ ) with PMMA coatings thicker depending on the type used ( $>10\text{\AA}$ ). The particles are doped with approximately 0.1-2.0 % and more in particular with 0.5-1.0% of dopant. A comparison of the properties of the nanocrystalline particles of the nanocrystals with bulk (non quantum sized) doped semiconductor powder is as follows:

Mn doped ZnS	Processing temperature	Mn- concentration	External Quantum Efficiency	Recombination Decay time
Nanocryst.	Room temp.	0.5 - 1.0%	18%	3 nsec.
Bulk	1100 C	1.0-2.0%	<20%	1.7msec.

Firstly, it is seen that the doped nanocrystals have an efficiency comparable to the bulk, yet they have been processed at room temperature while the bulk samples are annealed at temperatures  $>1000^\circ\text{C}$ . Secondly, in this size regime ( $\approx 33\text{\AA}$ ) a large percentage of atoms in nanocrystals are surface atoms which contribute to nonradiative recombination; in spite of this, the luminescent efficiency is high in these nanocrystals. The high efficiency of the doped nanocrystals when efficiency would normally be quenched by the nonradiative surface recombination is a unique property of encapsulated doped semiconductors and is not yet completely understood.

Fig. 4 illustrates the luminescent decay characteristics of a doped nanoparticle of the invention. In this test, the particles were illuminated by a short pulse of laser light and the intensity  $I$  (arbitrary units) of the light emitted with time in response is measured thereto at the characteristic wavelength of the activator element's (dopant) emission. As is seen in Fig. 4, the majority of the intensity peak is within only a few nanoseconds ( $<1 \times 10^{-8}$  seconds). A similar response for non-quantum sized powders which are chemically identical with the nanocrystals would be approximately a millisecond ( $1.7 \times 10^{-3}$  seconds). Put another way, the nanocrystal decay time is 10,000 to 100,000 times faster than the bulk material.

The materials described in this application can be improved by changing the starting compounds and their concentration. Samples with similar chemistries to those described when studied by transmission electron microscopy were about 65Å in size, whereas the best produced by homogeneous precipitation have been about 33Å and thus improvements in size reduction and enhancement of quantum confinement effects are possible. The Grignard exchange reaction to form diethylmanganese at step e may introduce unwanted residual byproducts to the solution. It has been seen in later experiments that the PMMA can be replaced by lower molecular weight polymer and even the methacrylic acid monomer whilst still retaining the quantum confinement of the surfactant. It is also apparent that other surfactants which meet the requirements stated above, may be more effective than those tried here.

In addition to the manganese doping of zinc sulfide the present process is also suitable for doping zinc sulphide with terbium, the starting component of the Grignard reaction is changed to  $\text{TbCl}_3$ . Additionally, other semiconductor host materials may also be prepared and doped with suitable activators. Such host

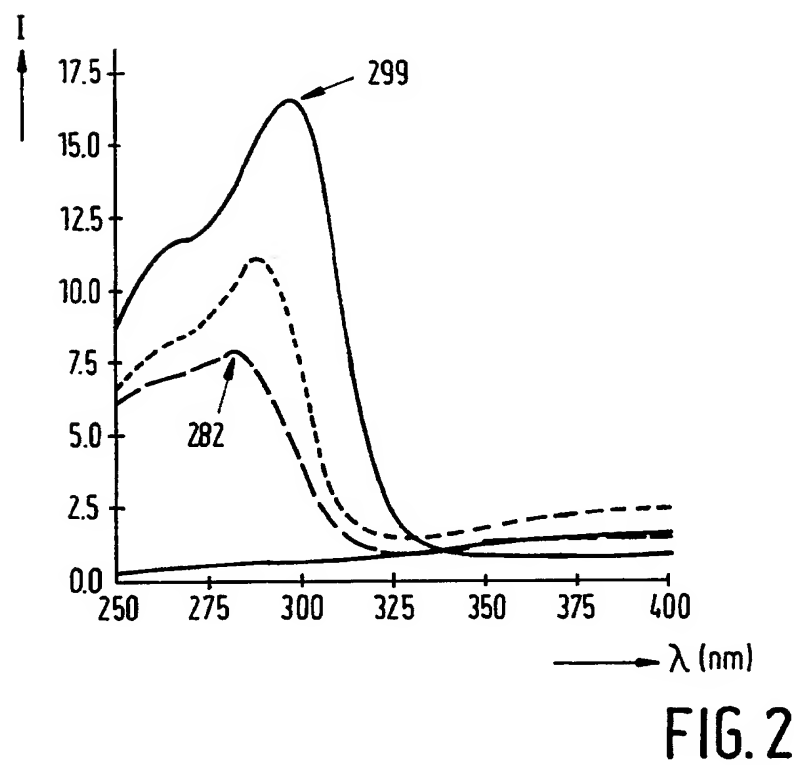
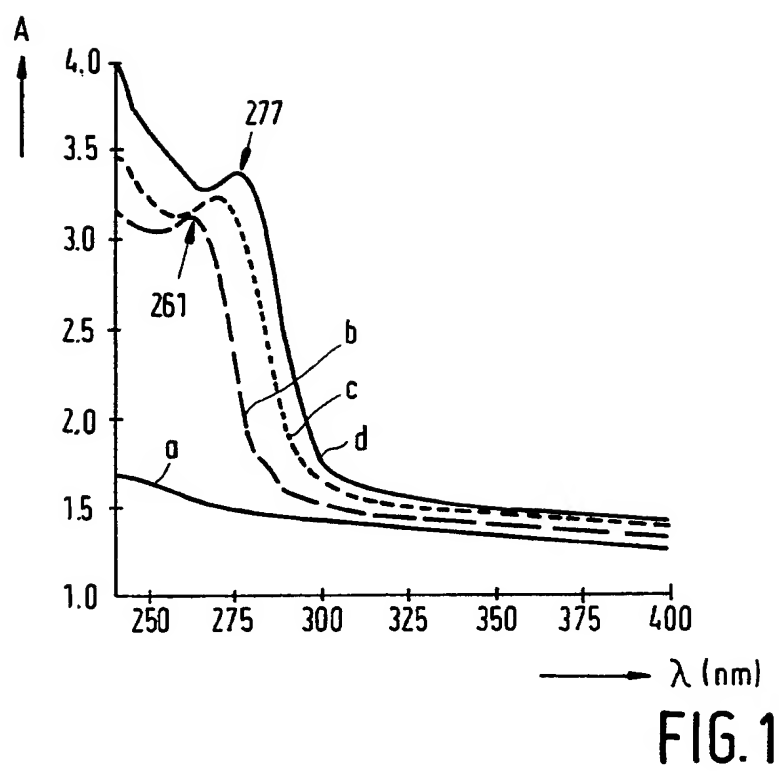
materials may be zinc selenide (ZnSe), zinc telluride (ZnTe), cadmium sulfide (CdS) and cadmium selenide (CdSe) and may also be created in similar reactions. Organometallic compounds containing these elements are either readily available or can be made by Grignard or other reactions. Finally dopants such as copper, silver, thallium, cerium, chromium, titanium, rare earths and other elements may be utilized.

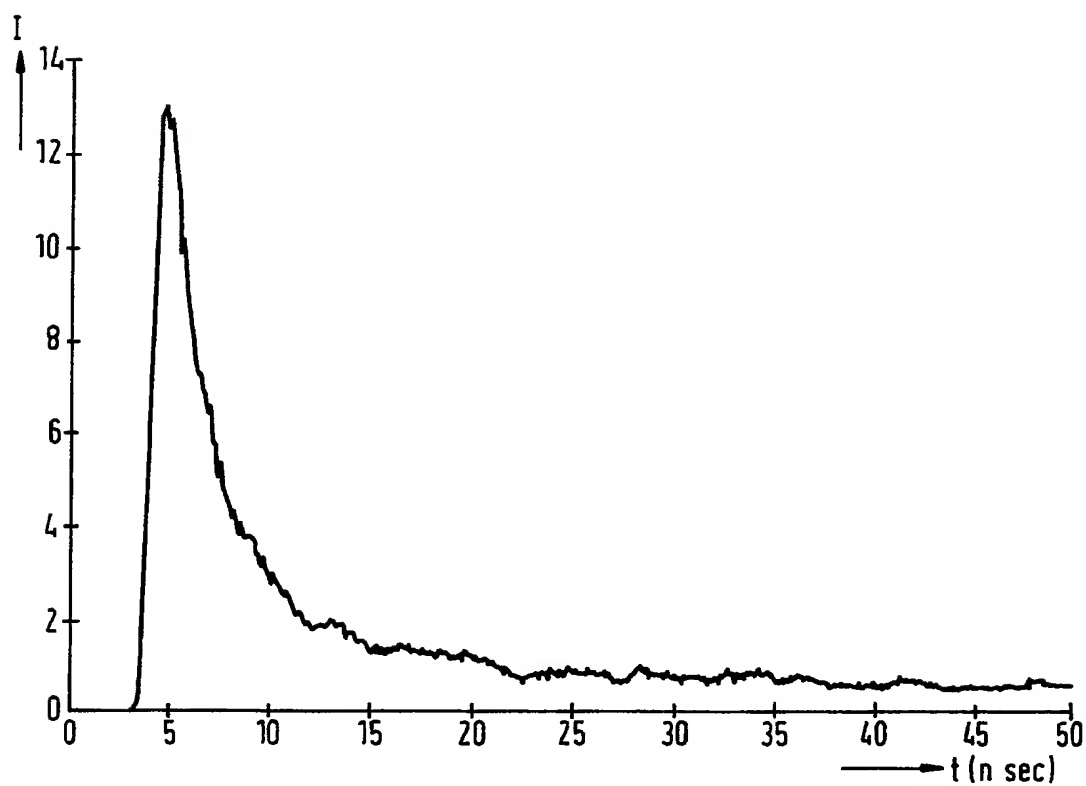
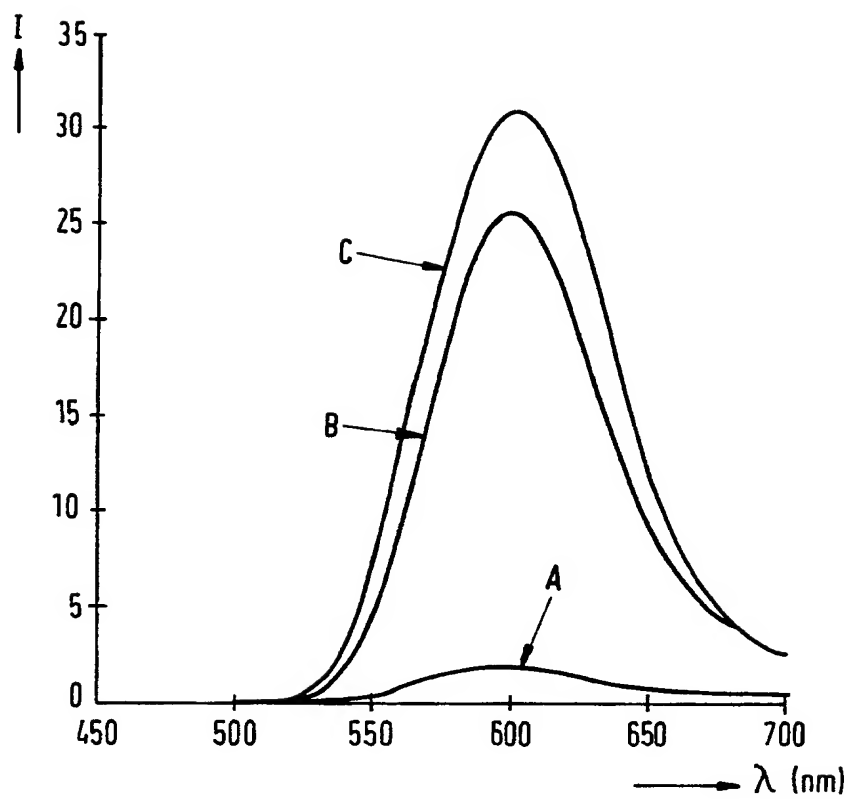
The organic solvent used in the reaction is Toluene. However, many other pure hydrocarbon solvents are also useable. Such suitable solvents are cyclohexane, hexane, heptane, octane and others. THF was used as the solvent in the Grignard reaction and other organic solvents may also be used. However, THF is known as being particularly effective in promoting Grignard reactions and is also soluble in with the Toluene used in the other reactions.

The above described arrangements and processing steps are merely illustrative of the principles of the present invention.

### Claims

1. An article of manufacture having a layer comprising particles of semiconductor material having a dopant incorporated therein, in which the particles have a size of less than 100 Å, said dopant is a phosphor activator, said particle is a phosphor host and said layer is an electroluminescent layer.
2. A doped particle of semiconductor material of less than 100 Å with a doping % of less than 2%.
3. A doped particle as claimed in Claim 2 wherein said doped particle comprises ZnS.
4. A doped particle as claimed in Claim 2 wherein said doped particle is disposed within a polymer matrix.
5. A doped particle as claimed in Claim 4 wherein said polymer matrix comprises polyethylene oxide.
6. A doped particle as claimed in Claim 2, coated with a surfactant.
7. A doped particle as claimed in Claim 6 wherein said surfactant comprises PMMA.
8. A doped particle as claimed in Claim 6 wherein said particle has been cured by exposure to UV light.
9. A doped particle as claimed in Claim 2, obtained by the steps of:
  - (a) dissolving a compound containing a first component of a host material, a compound containing a dopant and a matrix forming polymer in a first solvent;
  - (b) drying said polymer to form a matrix;
  - (c) immersing said polymer matrix containing said dissolved elements into a second solvent, said second solvent being incapable of dissolving said polymer matrix but capable of dissolving a compound containing the second component of said host material;
  - (d) dissolving a compound containing the second component of said host material in said second solvent to diffuse through the polymer matrix and to cleave said second component of the host material from said compound and growing said doped nanocrystals within said polymer matrix; and
  - (e) removing said polymer matrix from said second solvent and drying the matrix.
10. A doped particle as claimed in Claim 2, obtained by the steps of:
  - (a) dissolving in first organic solvent an organometallic compound containing a the first component of a host material;
  - (b) dissolving a surfactant in said first organic solvent;
  - (c) adding an organometallic compound containing a dopant to said first organic solvent;
  - (d) adding a compound which will provide the second component of the host material; and
  - (e) triggering the precipitation of doped particles which are coated with the surfactant.









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## EUROPEAN SEARCH REPORT

Application Number  
EP 94 20 1003

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. CL.5)
P,X	PHYSICAL REVIEW LETTERS, vol.72, no.3, 17 January 1994, USA pages 416 - 419 R.N.BHARGAVA & AL 'optical properties of manganese doped nanocrystals...' ---	1-3	C09K11/00 C09K11/57 H05B33/14 H05B33/18 H05B33/20
A,P	DATABASE INSPEC INSTITUTE OF ELECTRICAL ENGINEERS, STEVENAGE, GB Inspec No. 4528681 June 1993, P.D.PERSANS & AL 'size effects in II-VI semiconductor nanocrystals' * abstract *	1,2	
A	DATABASE INSPEC INSTITUTE OF ELECTRICAL ENGINEERS, STEVENAGE, GB Inspec No. 2755586 5 June 1986, L.BRUS 'Electronic wave fonctions...' * abstract *		
A	DATABASE INSPEC INSTITUTE OF ELECTRICAL ENGINEERS, STEVENAGE, GB Inspec No. 3902590 24 January 1991, Y.WANG & AL 'nanometer-sized semiconductors...' * abstract *		
			TECHNICAL FIELDS SEARCHED (Int. CL.5)
			C09K H05B
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 8 September 1994	Examiner Drouot, M-C
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	

## PATENT ABSTRACTS OF JAPAN

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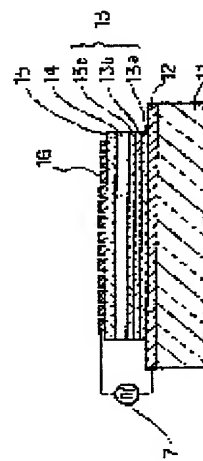
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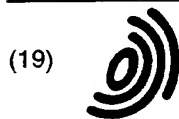
## (54) THIN FILM EL ELEMENT

## (57)Abstract:

**PURPOSE:** To realize high luminous intensity, high reliability, and high quality by providing a multifunctional insulating layer, which consists of a multi-layered film made of more than two different insulating films, for at least one of first and second insulating layers.

**CONSTITUTION:** A multifunctional layer which consists of a multi-layered film made of more than two different insulating films is provided at least one of first and second insulating layers. Namely, out of the first insulating layer 13 and the second insulating layer 15, a nitride film 13a is formed in contact with a transference electrode 12 (for example an ITO or the like) so that the blackening and increased resistance of the transference electrode 12 can be prevented and the improved luminous intensity can be achieved. And an insulating film 13c made of low resistance material formed under a luminescent layer 4 can increase the efficiency of electron injection into the luminescent layer 4, and further forming of the foundation layer of a luminescent layer 4 can improve the crystallization of the luminescent layer. On the top of the luminescent layer 4 is formed the same insulating film as an intermediate insulating film 13b as the second insulating layer 15. Thus, the luminous characteristics can be improved.





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(54) **Method and device for sealing of a thin film electroluminescent device**

(57) A method of forming a seal for a thin film electroluminescent device (10) includes using deposition techniques (36) to form an integral thin film encapsulating layer (26; 28). Plasma enhanced chemical vapor deposition is utilized, allowing the formation of the seal to take place at substantially room temperature. A pre-

bake (34) is performed at an elevated temperature in an evacuated environment prior to the formation of the thin film encapsulating layer. A silicon nitride film may be used as a single-film encapsulating layer, or may be used with another material (30) in the fabrication of a multi-film encapsulating layer.

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## Description

The invention relates generally to thin film electroluminescent devices and more particularly to a method and structure for hermetically sealing such devices.

Thin film electroluminescent (TFEL) devices are employed in a variety of applications. For example, an array of TFEL devices may be used to form a printhead. A conventional TFEL device includes an active semiconductor layer sandwiched between two dielectric layers. Electrode layers are formed on the surfaces of the dielectric layers opposite to the active semiconductor layer.

A TFEL device is typically driven by an alternating current signal. Light is generated when the potential difference between the two electrode layers reaches a threshold voltage. Electroluminescence occurs in the active semiconductor layer when electrical current is passed through the layer. The electrical current excites the dopant material, e.g. manganese. The selection of materials for forming the active semiconductor layer determines the frequency of light emitted from the TFEL device.

TFEL devices include an hermetic seal to protect the thin film layers, particularly the active semiconductor layer. The hermetic seal isolates the layers from contaminants and moisture which would adversely affect a TFEL device. The primary concern is film degradation due to exposure of the layers to moisture. Humidity significantly shortens the useful-life of a TFEL device.

U.S. Pat. Nos. 5,017,824 to Phillips et al. and 4,951,064 to Kun et al. describe sealing structures for forming contaminant-free environments for TFEL devices. A glass package is formed over the device to provide a chamber into which an oil is filled. For example, a silicon oil may be used.

While liquid-filled packages for TFEL devices have functioned well over the years, there are concerns. Firstly, a packaging assembly that requires forming and filling a leak-proof cavity adds significantly to the expense of a TFEL array. Moreover, the packaging interferes with establishing a simple array and lens system, and may complicate the task of achieving adequate lightbeam performance characteristics. Another concern is that such a package may adversely affect manufacturing yields of TFEL devices. Life-test results indicate widely varying results in seal integrity.

Attempts have been made to provide liquid-free seals for TFEL devices. U.S. Pat. No. 4,767,679 to Kawachi describes a seal comprised of an inner layer made of a thermoplastic resin and an outer, moisture-proof film that is heated and then press-bonded at its periphery to the substrate that supports one or more TFEL device. That is, the moisture-proof film must be aligned, heated and press-bonded to the substrate. U.S. Pat. No. 5,194,027 to Kruskopf et al. describes a seal formed by spreading a gel material over the active area of a TFEL panel and pressing a protective cover onto

the gel material so as to squeeze excess gel material from underneath the protective cover. The gel material is then cured to a predetermined degree of hardness. Finally, the protective cover is sealed against the TFEL panel with an adhesive vapor barrier. Another liquid-free seal assembly is described in U.S. Pat. No. 5,258,690 to Leksell et al. This seal assembly is an adhesive coating of solid clear material to encapsulate the light-emitting portion of the TFEL device.

While liquid-free seal assemblies of TFEL devices are known, the oil/glass packaging remains as the conventional assembly for hermetically sealing such devices. The concern with the known liquid-free seals involves the tendency of defects to propagate. In the industry, solid seals are considered to be less efficient in "self-healing," i.e. self-limiting with respect to propagation of burnouts caused by short circuits. The above-identified patent to Kruskopf et al., for example, identifies the concern of limiting the self-healing effects if the liquid-free packaging material covering the panel is too hard.

What are needed are a method and structure for forming the seal of a thin film electroluminescent device which reduce the expense and complexity of forming such a device without adversely affecting the manufacturing yield and/or the useful-life of the device.

## Summary of the Invention

Thin film deposition techniques are employed to form a thin encapsulating layer on a thin film electroluminescent (TFEL) device. In the preferred embodiment, the encapsulating layer is deposited utilizing chemical vapor deposition (CVD) techniques. Ideally, the thin encapsulating layer is deposited by plasma enhanced CVD, since such deposition allows the TFEL device to remain at a relatively low temperature during deposition. Moreover, plasma enhanced CVD is suitable for depositing an encapsulating layer of silicon nitride, with a low pinhole density and an adequate step coverage.

The first step is to form the TFEL device. While not critical to the invention, the conventional TFEL device includes an active semiconductor layer between two dielectric layers and opposed electrode layers. The five thin-film layers are formed on a substrate. It has been discovered that subjecting the TFEL device to a bake-out prior to depositing the encapsulating layer significantly improves the results of performance during life tests. That is, a greater percentage of devices exhibit desired performance characteristics if a pre-bake is performed in order to reduce moisture and other absorbed materials within the thin films to be encapsulated. The bake-out preferably takes place in an evacuated environment.

In the preferred embodiment, the TFEL device is an edge emitter device and the thin film encapsulating layer extends over the emitting edge. However, the utility of this invention is in no way limited to edge emission de-

vices, but may as readily be used on face emitting TFEL devices. Silicon nitride provides the desired properties, but silicon oxinitride, zinc sulfide plus silicon oxinitride, or aluminum nitride may be substituted.

The encapsulation is typically formed of a single layer. The bake-out is typically performed in an evacuated environment, but may be performed in a properly selected gas environment. However, multi-layer encapsulation is also contemplated.

An advantage of the invention is that a moisture-proof TFEL device may be formed without significantly increasing the expense or manufacturing complexity of the device.

#### Brief Description of the Drawings

Fig. 1 is a side sectional view of a thin film electroluminescent device formed in accordance with the invention.

Fig. 2 is a side sectional view of the thin film electroluminescent device of Fig. 1 having a thin film encapsulating layer in accordance with the invention.

Fig. 3 is a side sectional view of a second embodiment of an encapsulating structure in accordance with the invention.

Fig. 4 is an illustration of the method steps for forming the electroluminescent device of Fig. 3.

With reference to Fig. 1, a TFEL device 10 includes a multi-layer structure on a substrate 12. The substrate 12 may be formed of a transparent material, such as glass, but this is not critical.

A thin film active semiconductor layer 14 is sandwiched between an upper dielectric layer 16 and a lower dielectric layer 18. An acceptable material for forming the active semiconductor layer 14 is zinc sulfide that is doped with manganese. The dielectric layers may be silicon oxinitride, but other materials may be selected.

A drive signal is connected across an upper electrode layer 20 and a lower electrode layer 22. Typically, a TFEL device 10 is driven by an alternating current drive signal. Light is generated when the voltage across the TFEL device reaches a threshold voltage. Electroluminescence occurs in the active semiconductor layer 14 when electrical current is passed through the layer. The electrical current excites the electrons of the dopant material. The selection of materials for forming the active semiconductor layer determines the frequency of light emitted from the TFEL device.

The electrode layers 20 and 22 may be formed of indium tin oxide (ITO). ITO is an electrically conductive, optically transparent material for use in such applications as flat panel displays. Optionally, one or both of the electrode layers 20 and 22 may be optically opaque. In fact, in the preferred embodiment, the TFEL device 10 is an edge emitter device for radiating light from a forward edge 24. Edge emitter TFEL devices are designed to retard light radiation from the major surfaces of the devices. Typically, the substrate 12 supports an

array of TFEL devices, allowing the device to be used in such applications as printing.

Each of the layers 14, 16, 18, 20 and 22 is a thin film layer. "Thin film" is defined herein as a film having a maximum thickness of 15 microns. The layers may be formed using thin film deposition techniques known in the art. For example, electron beam evaporation or sputtering may be utilized.

Referring now to Fig. 2, an encapsulating layer 26 is deposited upon the upper surface of the TFEL device 10. In the preferred embodiment, the encapsulating layer is a silicon nitride layer deposited by plasma enhanced chemical vapor deposition (PECVD). An acceptable thickness is 4000 Å. PECVD utilizes radio frequency-induced glow discharge to transfer energy into a reactant gas, thereby allowing the substrate 12 to remain at a relatively low temperature. Room-temperature deposition is possible, so that the substrate and the layers 14-20 remain thermally stable during the formation of the encapsulating layer 26. PECVD is a technique in which deposited films have a low pinhole density and a good step coverage. Thus, the downward step from the upper electrode layer 20 to the surface of the substrate 12 is achieved without creating gaps.

Silicon nitride is the preferred material, but other materials may be substituted for forming the encapsulating layer 26. For example, silicon oxinitride, zinc sulfide plus silicon oxinitride, and aluminum nitride have been found to exhibit the desired characteristics for an encapsulating layer. Moreover, integrated circuit fabrication techniques other than PECVD may be used to form the encapsulating layer. Physical vapor deposition offers many of the same advantages afforded by PECVD.

If the TFEL device 10 is an edge emitter device and the encapsulating layer 26 is to cover the radiating surface, the encapsulating layer must be optically transparent. Moreover, the index of refraction of the encapsulating material must be considered. Preferably, the index of refraction of the encapsulating layer is matched to the index of refraction of the active semiconductor layer 14. Also, the thickness may be constrained by the desired spectra of the device. However, there may be some applications in which a mismatch achieves desired results.

Referring now to Fig. 3, in a second embodiment, the encapsulating layer is a multi-film structure. A lower film 28 may be selected for its desired characteristics with respect to hardness. An upper, capping film 30 can then be formed to fill and/or cover any pinholes that may be created during the deposition of the lower film 28. In this manner, the moisture impermeability of the structure is improved. As an example, a polycrystalline material, such as zinc sulfide, which has been shown to have excellent resistance to pinhole formation, or polymeric materials may be used to form the lower film 28. The capping film 30 may then be silicon nitride. Capping of polymeric films under controlled-stress conditions is possible, because of the use of a room-temperature deposi-

tion system.

Referring now to Fig. 4, the steps of fabricating the structure of Fig. 3 begin with the formation 32 of a TFEL array. This step may be performed using any of the known techniques for forming thin films on a substrate. In the preferred embodiment, the TFEL array is then subjected to a bake-out 34. For example, a 30-minute bake-out at 250°C in an evacuated environment has been used to fabricate TFEL arrays in which a high percentage of light-emitting devices have survived a life test of more than 1000 hours at 45°C and 85% relative humidity. The bake-out at an elevated temperature in an evacuated environment provides outgassing that acts against sealing in moisture or other volatile substances when the encapsulating layer is introduced. The bake-out may also be performed in a controlled gas environment.

Still describing the preferred embodiment, PECVD encapsulation 36 seals the TFEL array. The bake-out step 34 and the physics of PECVD substantially overcome the problem of propagating defects typical of prior art solid sealing structures. The final step is one of depositing 38 the capping layer. However, the PECVD encapsulation may be a step that takes place after formation of a lower layer in a multi-film encapsulating structure.

#### Claims

1. A method of forming a seal for a thin film electroluminescent device (10) comprising the steps of:

providing a thin film electroluminescent device having a plurality of layers (14, 16, 18, 20 and 22), including an active semiconductor layer (14), said thin film electroluminescent device having a first surface; and

using integrated circuit fabrication techniques (36) to encapsulate said thin film electroluminescent device, including forming an integral thin encapsulating layer (26; 28) on said first surface and on at least one edge (24) of said thin film electroluminescent device such that said active semiconductor layer is sealed from a surrounding atmosphere by said thin encapsulating layer formed using integrated circuit fabrication techniques.

2. The method of claim 1 wherein said step of using integrated circuit fabrication techniques (36) to encapsulate said thin film electroluminescent device (10) includes forming (38) at least one additional thin film layer (30) atop said integral thin encapsulating layer.
3. The method of claim 1 or 2 wherein said step of forming said thin encapsulating layer (26; 28) in-

cludes utilizing chemical vapor deposition techniques (36).

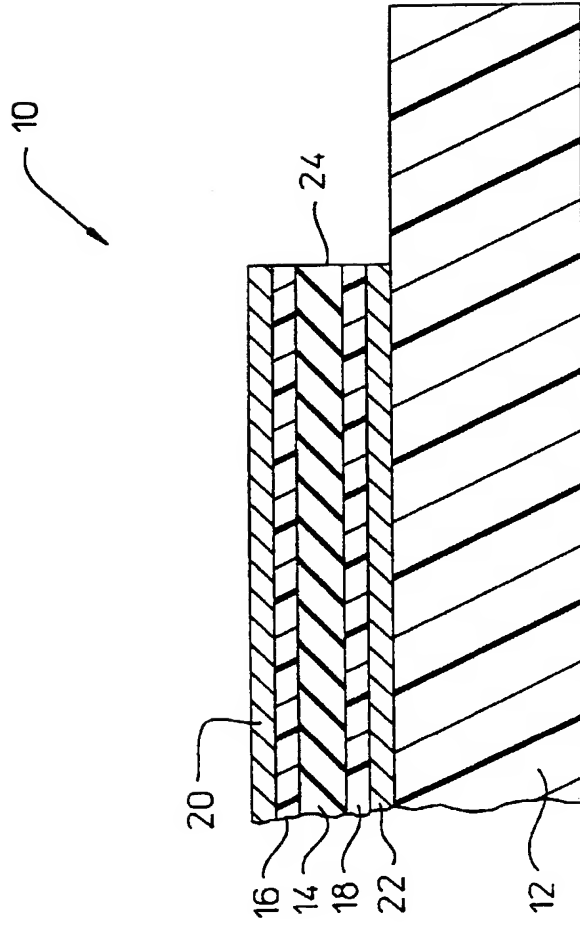
4. The method of claim 1 or 2 wherein said step of forming said thin encapsulating layer (26; 28) includes utilizing physical vapor deposition techniques.
5. The method of claim 1, 2, 3 or 4 further comprising pre-baking (34) said thin film electroluminescent device (10) prior to said step of forming said thin encapsulating layer (26; 28), said pre-baking being performed in an evacuated environment and at elevated temperatures.
6. The method of claim 1, 2, 3 or 4 further comprising pre-baking (34) said thin film electroluminescent device (10) at elevated temperatures and in a dry environment prior to said step of forming said thin encapsulating layer (26; 28).
7. The method of claim 3 wherein utilizing chemical vapor deposition techniques (36) includes plasma enhanced chemical vapor depositing a dielectric material (26; 28).
8. An electroluminescent device (10) comprising:

a substrate (12);

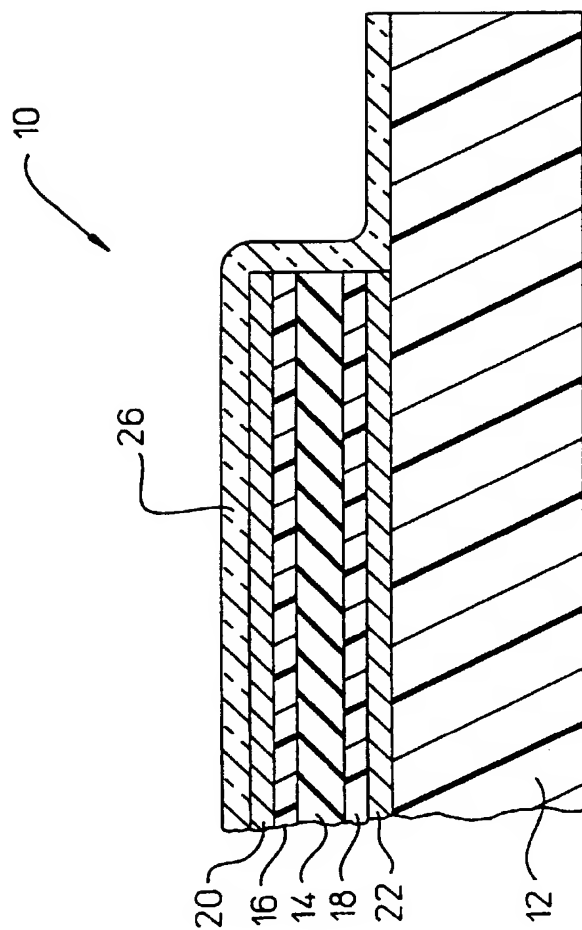
a layer stack (14, 16, 18, 20 and 22) supported on said substrate, including a thin film active layer (14) which generates light in response to conduction of electrical current and first and second thin film electrode layers (20 and 22) on opposed sides of said active layer, at least one of said electrode layers being spaced apart from said active layer by a thin film dielectric layer (16 and 18); and

a thin film encapsulating layer (26; 28) formed on said layer stack, said encapsulating layer being a nitride layer, said encapsulating layer extending across said layer stack on a side opposite to said substrate and coating at least one edge (24) of said active layer to seal said edge from a surrounding atmosphere.

9. The device of claim 8 wherein said encapsulating layer (26; 28) is silicon nitride.
10. The device of claim 8 further comprising a capping layer (30) coating said encapsulating layer (28), said capping layer being formed of a material that is substantially moisture-imperious.

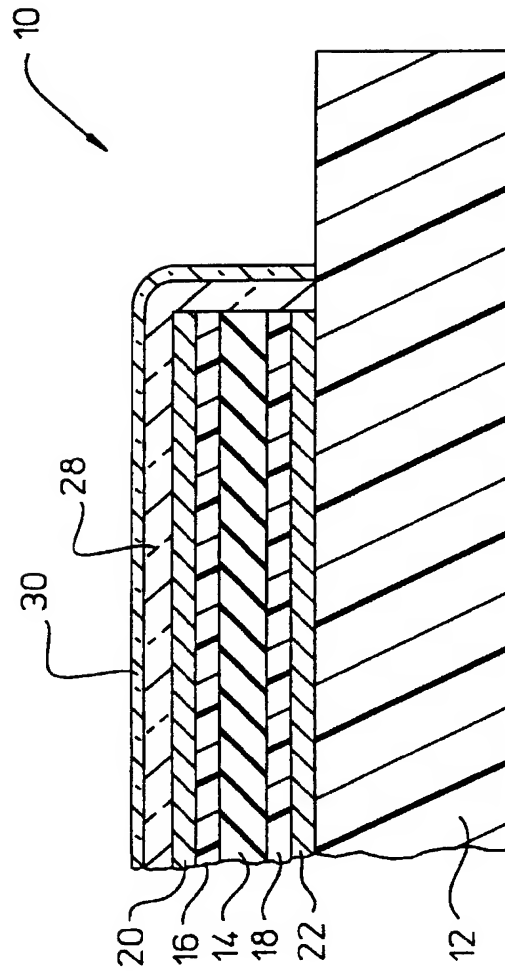


**FIG. 1**

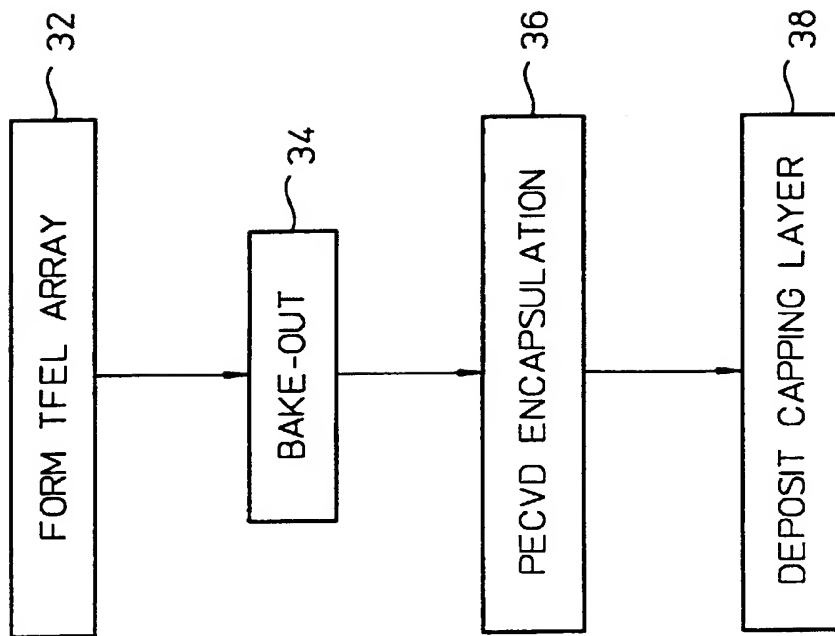


**FIG. 2**





**FIG. 3**



**FIG. 4**